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EFFECTS OF ACID DEPOSITION ON PAINTED WOOD SUBSTRATES

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This report describes the progress that has been made within the Coatings Effect Research Program that EPA conducts for Task Group VII within the National Acid Precipitation Assessment Program (NAPAP). The major objective of this phase of the research program is to identify early failure processes associated with acidic deposition on painted wood substrate systems. Effects that have been observed during short term accelerated exposure studies are as follows: (1) FTIR, NMR, and Sol- gel analysis indicate that SO_2 attacks the base terpolymer of latex polymeric coating in the presence of UV radiation. This polymer is stable upon exposure to SO_2 alone, either gaseous or aqueous as sulfurous acid, (2) Sulfurous acid diffuses through both oil-alkyd and latex coatings and can degrade lignin of the wood substrate, (3) Field and laboratory studies indicate that $CaCO_3$ & ZnO are removed from latex paints during exposures. The removal rate decreases with increasing pH, and (4) Discoloration or yellowing of $CaCO_3$ containing paints on wood substrates has been observed after three months field exposure. Based on the findings, it is recommended that research be continued to develop dose response relationships for the effects of acid deposition on coated wood substrate systems.

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ABSTRACT

This report describes the progress that has been made within the Coatings Effect Research Program that EPA conducts for Task Group VII within the National Acid Precipitation Assessment Program (NAPAP). The major objective of this phase of the research program is to identify early failure processes associated with acidic deposition on painted wood substrate systems. Effects that have been observed during short-term exposure studies are as follows:

- Fourier-transform infrared, nuclear magnetic resonance, and sol-gel analyses indicate that SO_2 attacks the base terpolymer of latex polymeric coating in the presence of UV radiation. This polymer is stable upon exposure to SO_2 alone, either gaseous or aqueous as sulfurous acid.
- Sulfurous acid diffuses through both oil-alkyd and latex coatings and can degrade lignin of the wood substrate. The loss of strength of the coating-wood interface is being investigated by using fracture mechanics.
- Field and laboratory studies indicate that $CaCO_3$ and ZnO are removed from latex paints during exposures. The removal rate decreases with increasing pH. The latex paint film collapses to fill voids as $CaCO_3$ is removed.
- Discoloration or yellowing of $CaCO_3$-containing paints on wood substrates has been observed after three months of field exposure.

On the basis of the findings, it is recommended that research be continued to develop dose-response relationships for the effects of acid deposition on coated wood substrate systems.

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CONTENTS

Abstract		iii
Figures		vi
Tables		vii
1.	INTRODUCTION	1
2.	TECHNICAL APPROACH	5
	Polymer Molecular Investigations	5
	Solubility and Diffusivity Measurements	6
	Characterization of the Paint-Wood Interface	8
3.	RESULTS AND DISCUSSION	12
	Molecular Structure Studies	12
	Permeability and Chemical Structure Studies	14
	Paint Wood Interface Studies	19
4.	CONCLUSIONS	24
5.	RECOMMENDATIONS	26

Figures

Number		Page
1.	GPC Chromatogram of Base Acrylic Polymer	28
2.	Sorption isotherms for SO_2 in Paint Samples at 28°C	29
3.	Diffusivity of SO_2 in Paint Samples at 28°C	29
4.	Weight Loss of $CaCO_3$ from Latex Paint Samples in Sulfurous Acid	30
5.	FTIR-ATR Spectra from Latex Paint Samples Exposed to pH 2.0 Sulfurous Acid	30
6.	Relative Infrared Peak Intensities for Latex Paint Immersed in pH 1.3 Sulfurous Acid	31
7.	EDS of the Cross Section of WRC Panels Treated with Sulfurous Acid Showing Elemental Constituents Just Below Paint-Wood Interface	32
8.	EDS Line Scan of Sulfurous-Acid-Treated SP Panels Painted With One Coat of Acrylic Latex Primer and Two Topcoats	32
9.	EDS of Paint Wood Interface of WRC Painted With Oil-Alkyd Primer and Topcoat	33
10.	^{13}C-NMR of Lignin Extracted from WRC Treated with Sulfurous Acid	34
11.	Typical Structure for Softwood Lignin: Structure of Model Compounds Shown in Boxes	35
12.	Adhesive Strength of Painted Specimens Exposed at 100 ppm Sulfur Dioxide for up to 8 Weeks and Their Matched Controls	36

TABLES

Number		Page
1.	Composition (% by weight) of Paints	37
2.	Properties of the Base Polymer of A Latex Paint Upon Exposure to $SO_2/H_2O/UV$ Combinations	38
3.	Solubility, Diffusivity and Permeability at Typical Atmospheric Levels of SO_2	39

SECTION 1

INTRODUCTION

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) of the U. S. Environmental Protection Agency (EPA) is conducting a program, Effects of Acid Deposition on Materials, that is planned by Task Group VII, Effects on Materials and Cultural Resources. This task group is one of several groups that are conducting research within the National Acid Precipitation Assessment Program (NAPAP). Within Task Group VII, EPA has the responsibility for studying effects on materials of construction, primarily metals and paints, whereas the National Park Service and U.S. Geological Survey are studying cultural stone materials. One of the primary missions of Task Group VII is to provide NAPAP and EPA with scientific data on the cause and effect relationships (damage function models) of acid deposition on man-made and naturally occurring materials. These models will be used by NAPAP to evaluate the economic loss associated with acid deposition damage to materials. Because of their economic importance and exposure to acid deposition, exterior coatings are one of the types of materials that Task Group VII and EPA is interested in studying.

Before beginning a study of exterior coatings, EPA held a workshop to review a planning document entitled " Research Plan for Determining the Effects of Acid Deposition on Exterior Coatings" (1). The plan was approved in January 1987. In addition to this document, EPA had prepared an internal report entitled "Strategy and Documentation for Conducting Research on the Effects of Acid Deposition on Coating-Substrate Systems:

The Data Quality Objective Process" which supplements the research plan and provides guidance to researchers who are conducting effects research on coating-substrate systems. These two documents provide the cornerstone for the coatings research program.

This report reviews the progress that has been made under Task 3 of the research plan conducting preliminary exposure studies in which analytical techniques are used to identify early failure processes associated with acidic deposition on coated wood substrate systems. Task 3 as proposed in the plan is now completed. The report recommends Task 4 of the research plan which involves conducting field and exposure chamber studies from which dose-response functions can be derived for predicting the effects of acidic deposition on the film failure processes be initiated.

A summary of the damage to coated-wood substrate systems that were observed during the Task 3 short-term accelerated exposures to acidic deposition is as follows:

A. Structural and Property Effects

- It has been shown that SO2 in the presence of UV radiation reacts with films of the base acrylic terpolymer of the latex paint, thus accelerating the rate of degradation. A number of competing reactions cause major microstructural changes in the polymer. These changes affect the paint film properties as follows:

    1. Dramatic increase in the glass transition temperature
    2. Large increase in the gel fraction
    3. Extensive polymer backbone chain scission
    4. Loss of the acetate side groups
    5. Dehydrodehalogenation
    6. Discoloration
    7. Increase in the surface polarity

B. Solubility and Permeability Characteristics

- SO_2 has relatively high solubility and permeability in acrylic latex and alkyd paints. If these paints are applied on on substrates that can react with and/or absorb SO_2 then rapid diffusion of SO_2 is observed.

- In the absence of UV, essentially all absorbed SO_2 in latex films is removed upon desorption while a significant amount of SO_2 (about 10-20% of the amount absorbed) is retained in alkyd films.

C. Dissolution of Particles

- Both laboratory and field studies confirm that dry deposition of acid gases such as SO_2 and HNO_3 dissolves alkaline compounds (e.g. $CaCO_3$, ZnO) in paint films, and that acids deposited during precipitation causes additional dissolution.

- Quantitative data for the rate of removal of $CaCO_3$ from latex paint films have been obtained as a function of pH. As the pH decreases, the rate of $CaCO_3$ removal increases dramatically. $CaCO_3$ removal from a latex paint film is accompanied by a collapse of the polymer to fill voids created by the dissolution of the $CaCO_3$ particles, resulting in a decrease in the film thickness and an increase in the solubility and permeability of gases in the film.

- After three month exposure at the North Carolina and Ohio field sites, discoloration or yellowing of $CaCO_3$ containing paints on wood substrates is being observed.

- Leaching of alkaline particles also causes dimensional changes in the film. If the film is on a substrate, these changes may result in local stresses at the paint substrate-interface.

D. Effects on Wood Substrates

- The weathering of wood prior to painting decreases paint adhesion. Sulfurous, sulfuric, and nitric acids increase the rate of weathering significantly.

- SO_2 and sulfurous acid readily diffuse through the coatings and are absorbed by wood. Recent studies have shown that the sulfur compounds accumulate primarily at the paint wood interface.

- A significant amount of SO_2 is retained in the wood following sorption-desorption. SO_2 is likely reacting with the lignin of wood.

- Lignin model compounds that were encased in paint films de-

graded within several weeks of exposure to either gaseous SO_2 or sulfurous acid.

SECTION 2

TECHNICAL APPROACH

Three paints were specially formulated and supplied to initiate the exposure study under Task 3 of the research plan (1).

- Acrylic latex paint containing $CaCO_3$
- Acrylic latex paint without $CaCO_3$
- Alkyd gloss paint.

Also supplied was the base polymer used to formulate the latex paints. The composition of the paints is shown in Table 1. The formulations of each paint were recommended and prepared by a national manufacturer of paints and ingredients. Other commercial paints may be added to this study pending a report on commercial coatings and substrate that is called for within the coatings research plan (1).

POLYMER MOLECULAR INVESTIGATIONS

A cylindrical Rayonnet UV reactor with 350-nm lamps was modified to allow air/H_2O/SO_2 and/or NO_2 mixtures to pass through quartz reactor tubes inside the chamber. Following exposure to various atmospheric conditions, free film samples were examined by using a variety of analytical techniques. The techniques that were used to measure physical property and chemical structural changes during exposure are as follows:

1. Sol-gel analysis and intrinsic viscosity measurements of the soluble portion: to obtain information about the relative amount of cross-linking vs. chain scission of the polymer chains. Cross-linking causes embrittlement, and scission causes a loss of mechanical strength and stiffness). The soluble fraction was obtained by immersing films in tetrahydrofuran for three days and then separating the soluble fraction from the insoluble fraction by filtration.

The fractions were recovered by evaporation of the solvent. Intrinsic viscosity measurements were determined at 25°C.

2. Gel permeation chromatography (GPC) of the soluble portions: to follow the distribution of molecular weight of the polymer. The GPC results were obtained by using a differential refractometer.

3. Solid state and high-resolution ^{13}C-NMR: to follow chemical changes in the entire film and in the soluble and insoluble portions.

4. Contact angle measurements: to measure the change in the surface polarity with distilled water as the contact liquid.

5. Dynamic mechanical analyses (DMA): to measure the change in the glass transition temperature (T_g) and the dynamic elastic modulus.

6. Differential scanning calorimetry: to measure heats of fusion and to obtain an independent measure of the T_g.

7. X-ray photoelectron spectroscopy: to measure charge in the surface chemistry.

A more detailed description of these techniques as well as other techiques that are being investigated has been previously reported (2). These techniques were used in our research, which has emphasized the effects of acid pollutants in combination with H_2O and UV light on a base latex polymer without paint compounding ingredients. Experimental results for each exposure treatment are based on multiple sets of data.

SOLUBILITY AND DIFFUSIVITY MEASUREMENTS

Solubilities and diffusivities of gases in polymer or paint films can be conveniently measured using the well-established weight gain method. The sample consists of a thin film (0.5-4 mil) suspended on a weight-sensitive device, such as an electrobalance or quartz spring, which is enclosed in a glass vacuum chamber. After degassing the sample, the gas is introduced at some fixed temperature and pressure. The sample weight is monitored continuously as the gas diffuses into the sample.

Analysis of the sorption kinetics using appropriate solutions to the time-dependent diffusion equation yields the diffusion coefficent (D). For diffusion into (out of) a thin film at short times, the following equation applies:

$$\frac{M_t}{M\infty} = \frac{4}{l} \left(\frac{Dt}{\pi}\right)^{0.5} \qquad (1)$$

where M_t is the weight gained (lost) at time t, $M\infty$ is the equilibrium weight gain (loss), and l is the film thickness. D is therefore obtained from the initial slope of a plot of $(M_t/M\infty)$ vs. $(t)^{0.5}$.

A plot of the equilibrium sorbed concentration ($C=M\infty$) vs. pressure at constant temperature produces a sorption isotherm. Sorption isotherms for gases in polymers above their glass transition temperature (T_g) are linear (i.e., Henry's law behavior). Our measurements to date indicate that sorption isotherms for paints fall into this category (3). The slope of this isotherm is the solubility (S) of the gas in the polymer. The permeability (P) can then be calculated from its definition: P = SD. Desorption measurements can also be made by evacuating the system and monitoring weight loss on a sample previously equilibrated with gas. The occurrence of a chemical reaction between the sample and the gas can be inferred if all of the sorbed gas cannot be removed under vacuum.

Highly soluble gases such as SO_2 tend to plasticize the polymer at relatively low sorption pressures. Plasticization usually facilitates diffusion, resulting in a concentration-dependent diffusivity and permeability. The concentration (C) dependence is often exponential:

$$D = D_0 \exp(AC). \qquad (2)$$

Here D_0 represents the infinite-dilution diffusivity, and A is the so-

called plasticization parameter. The concentration dependence of D and P disappears at a sufficiently low sorbed concentration or pressure. Typical maximum atmospheric levels of SO_2 (10-30 ppb) are well within the concentration-independent regime, but the sorbed concentrations of SO_2 in paint samples at these SO_2 pressures are impossible to measure with weight gain methods. This difficulty is easily overcome by extrapolating plots of ln(D) vs. C to zero concentration. The intercept, D_0, represents the diffusivity which would apply at typical atmospheric SO_2 levels. The corresponding permeability at infinite dilution is then obtained by multiplying D_0 by the (pressure-independent) solubility, S.

Fourier-transform infrared attenuated total reflectance (FTIR-ATR) has been used to assess changes in chemical composition of the paints. Techniques have been developed that permit measurement of diffusion of water and acidic ions into the films, and simultaneously detect changes in the composition of the films induced by the absorbed acids. FTIR-ATR has also been used in a more routine manner to characterize any degradation of the polymer binder in the paints after exposure to various weathering histories.

CHARACTERIZATION OF THE PAINT-WOOD INTERFACE

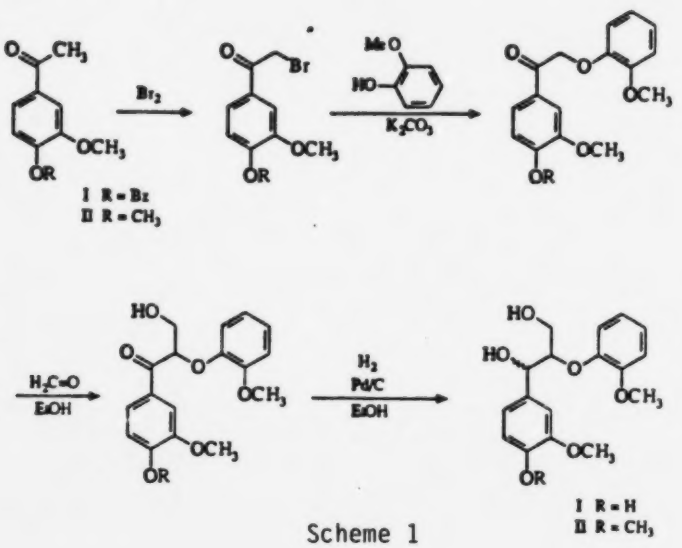
Western red cedar (WRC) and southern pine (SP) strips coated on all sides with alkyd or acrylic latex paint were soaked for 10 days at room temperature in sulfurous acid, sulfuric acid, sodium sulfite, or sodium sulfate solutions. Matched controls were soaked in distilled water. After exposure to acid or salt solutions, cross sections of the specimens were analyzed for sulfur compounds in the paint and wood using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

The detection of sulfur at the paint-wood interface may indicate wood or paint degradation.

Chemical Analysis

This work included examination of lignin exposed to sulfurous acid, analysis of carbohydrate degradation products (sugar), acid treatment of unpainted wood, and examination of lignin model compounds and wood encapsulated in paint film.

The analytical techniques will include sugar analysis to evaluate carbohydrate degradation, inductively coupled plasma to measure sulfur content, and ^{13}C-NMR spectrum to evaluate chemical changes in the ^{13}C-NMR spectrum of lignin is extemely complex; however, many parts of the spectrum have been previously elucidated through the study of model compounds (7). The objective of our initial investigation will be to identify the major degradation products of the model compounds exposed to sulfurous or sulfuric acids. The salient features of the ^{13}C-NMR spectra will be used to identify similar degradation products from wood exposed to similar conditions. The models chosen are guaiacyl glycerol - guaiacyl ether [1 (3-methoxy-4-hydroxy)-2-(2-methoxyphenoxy)-propane-1,3-diol] synthesized as shown by Scheme 1 as a mixture of the threo and erythro forms and the 4-methoxy analog (II). These compounds closely model the -aryl ether moiety, the most common linkage found in lignin. The results from the model studies will be used to interpret the ^{13}C-NMR spectra obtained from lignin isolated from WRC panels exposed to acid. These experiments included both unpainted wood and wood encapsulated in a precast paint film.



Scheme 1

Mechanical testing

The WRC panels with the same finish used for chemical analysis are being subjected to similar exposure to acids under laboratory conditions. Adhesion testing of these panels is used to link paint performance criteria with chemical degradation of the interface. Unpainted and painted wood are exposed to either high SO_2 concentrations (100 ppm) in a flow chamber or intermittent sulfurous acid soaking during accelerated weathering. In initial studies, panels were exposed to SO_2 in a 6-mph wind chamber for up to five weeks. The chamber recycled the air-SO_2 mixture and had a complete change of atmosphere every hour. The relative humidity (RH) was cycled between 20% and 80%. Specimens were removed and placed in 65% RH after 1, 2, 3, and 5 weeks. A set of controls received the same treatment without SO_2. After exposure, all specimens were equilibrated at 65% RH for several weeks and tested for paint adhesion by using lap-shear and fracture mechanics techniques.

In January 1988, field exposures of painted wood specimens were in-

itiated at the NAPAP material exposure sites at Steubenville, OH, Research Triangle Park, NC and Madison, WI. The first set of panels will be removed in June 1989. A small portion of the removed panel will be analyzed by EDS for sulfur content. Paint adhesion will be determined and the paint-wood interface analyzed for decomposition products using ^{13}C-NMR. If paint adhesion is not significantly different from that of the control, degradation will be evaluated by difference in degradation products. We hope to identify the decomposition products isolated from the paint-wood interface and compare them with products obtained from the laboratory exposure experiments.

SECTION 3

RESULTS AND DISCUSSIONS

MOLECULAR STRUCTURE STUDIES

The polymer chosen for our investigations was an acrylic latex prepared by a major producer of acrylic emulsion latex. It is a polymer made from equimolar amounts of butyl acrylate, vinyl acetate, and vinyl chloride and also a small amount of methyl methacrylate. A nonuniform, continuous monomer feed is used to compensate for differences in monomer reactivity ratios. The polymer has a multimodal molecular weight distribution, as illustrated in Figure 1A. Cross-linking also occurs during the polymerization as the polymer has an initial gel content of 22%.

Because the acrylic latex base polymer provides the mechanical strength and structural integrity of a paint film, it is the most essential component in an organic paint coating that protects a substrate. The investigations on the polymer involved short-term tests to explore whether or not the base polymer is attacked by acid pollutants in the atmosphere and to assess in an expeditious manner the mechanistic aspects of polymer microstructural change causing polymer degradation. The results shown below clearly demonstrate that significant detrimental effects are observed when the polymer is exposed to certain combinations of pollutants.

Shown in Table 2 are representative results of effects of exposure in the Rayonnet UV reactor of the base latex polymer employed in our investigations. The variations include: exposure up to 96 h to SO_2, SO_2/UV,

$SO_2/UV/H_2O$, SO_2/H_2O, and $UV/air/H_2O$. Data are presented for surface contact angles, the sol-gel fraction, and the viscosity of the soluble fraction. The most rapid increase in gel fraction occurs when samples are exposed to a combination of UV and SO_2.

As shown in Table 2, exposure to SO_2 alone, either in the presence or absence of moisture, has little or no effect on film microstructure or properties. Upon exposure to UV alone, there is a rapid increase in gel content and a decrease in the viscosity of the soluble portion, indicating both cross-linking and chain scission are occurring. In the presence of moisture, cross-linking is suppressed, and chain scission is reduced upon exposure to UV. There is essentially no change in the glass transition temperature or surface contact angle at the polymer upon exposure to either UV or SO_2 alone in the absence of moisture. In the presence of moisture and UV or SO_2 alone, there is an increase in the surface contact angle, but the glass transition temperature decreases at 96 h indicating that chain scission is rapid under these conditions. UV/SO_2 exposure causes an initial rapid increase in gel content, leveling off around 60-70%, both in the presence and absence of moisture, and chain scission is also rapid - particularly in the presence of moisture. However, dramatic changes occur in the glass transition temperature and in the molecular weight of the soluble fraction with UV/SO_2 exposure, both with and without the presence of moisture.

Dynamic mechanical analyses of the base acrylic film and several samples exposed under different conditions illustrate the effects. The DMA spectra clearly show the dramatic increase in the glass transition

temperature with exposure to UV/SO_2, indicating an embrittled structure developing. Also, the modulus remains relatively high, well above ambient temperature. These data suggest that effects of cross-linking are significant in this case.

Figures 1A, B, and C show the GPC data of the soluble fraction of the control and several samples exposed under different conditions, illustrating effects on the molecular weight of the polymer. The molecular weight of the polymer increases as the elution time decreases. The peaks in the GPC data indicate the presence of a multimodal and broad molecular weight distribution. Upon exposure, the changes in peak positions and relative intensity suggest that there are specific components in the polymer that react preferentially with excited SO_2.

^{13}C-NMR spectra of selected films and fractions of the polymer were also obtained as a function of exposure. Changes in the spectra are indicative of specific chemical attack on the polymer. The ^{13}C-NMR shows that the peak at 170 ppm (which is assigned to the vinyl acetate carbonyl carbon based on homopolymer spectra) decreases significantly when the film is exposed to UV/SO_2 but changes negligibly in the presence of UV alone. A weak peak occurs around 130 ppm, which is associated with unsaturated groups due to the formation of HCl and acetic acid from the polyvinyl chloride and the polyvinyl acetate, respectively. Also a new peak forms at 75 ppm, which is tentatively assigned to the formation of a sulfur-carbon bond. Independent verification of the attack on the vinyl acetate group when the films are exposed to UV/SO_2 has been obtained by FTIR (2).

PERMEABILITY AND CHEMICAL STRUCTURE STUDIES

Solubilities

The solubilities of SO_2 at 28°C in each of the paints and the base polymer were obtained over a pressure range of 50-700 torr SO_2. As shown in Figure 2, each sample exhibited linear behavior, following Henry's law. The solubilities have been listed in Table 3, column 2. The SO_2 solubility is quite high; the polymer base absorbs about 14% by weight of SO_2 at 760 torr. The solubility of SO_2 in the alkyd paint is nearly identical to the latex paints. The isotherms nearly superimpose when the amount of SO_2 sorbed by the paint samples is normalized to the amount of polymer in the paint (~37 wt.%). This indicates that sorption occurs only in the polymer, with the inorganic additives acting as impenetrable fillers.

Diffusivities

Diffusion coefficients for SO_2 in the four samples are plotted against pressure in Figure 3. Exponential concentration dependence (Eq. 2) is followed. Extrapolation to zero concentration (zero pressure) yields D_0; these values have been listed in Table 3, column 3. Diffusivities are highest for the latex base polymer, which has no filler particles to interfere with the movement of molecules through the polymer. The two latex paints have nearly identical SO_2 diffusivities, and the values for the alkyd paint are about an order of magnitude lower, as expected for a cross-linked polymer. The concentration dependence of D disappears at about 50 torr SO_2 for all samples. The slopes of the lines in Figure 6 are related to the degree of plasticizability of the samples. The latex samples behave similarly, whereas the alkyd sample has a higher slope, indicating that it can be plasticized to a larger extent by a given amount of sorbed SO_2.

Permeabilities

The permeabilities follow the same trend as the diffusivities, increasing exponentially with increasing concentration. The permeabilities at infinite dilution, calculated from $P_0 = SD_0$, have been listed in Table 3, column 4. These values would be applicable at typical atmospheric levels of SO_2. As shown in Table 3, the latex paints show a much larger permeability to SO_2 than the alkyd paint. The total flux, J, of gas through a film of thickness l exposed to a penetrant pressure difference of Δp can be calculated from the permeability as:

$$J = \frac{P\Delta p}{l}$$

Desorption Experiments

Desorption measurements were carried out with each sample at each pressure to determine how much SO_2 (if any) remained in the paint samples. For the latex paints and latex base polymer, it was possible to remove all of the sorbed SO_2 and recover the original sample weight (to within a few micrograms, the precision of the weighing system). However, it was found that a 150 mg-alkyd sample retained approximately 0.5 mg of the 3.0 mg of SO_2 it had absorbed at 223 torr, even after exposure to a vacuum of less than 1 mtorr over several days. This is a significant fraction (17%) of the total amount absorbed, and is well above the minimum detectable weight change (~0.01 mg) for our sorption system. This suggests that SO_2 is chemically reacting with the alkyd paint.

$CaCO_3$ Leaching

Other investigators have found evidence of removal of $CaCO_3$ extender from paints upon exposure to acid rain conditions, in both field and chamber studies (8). We have quantified the rate of removal of $CaCO_3$ with both weight loss and FTIR-ATR measurements. Acrylic latex paint films, with and without $CaCO_3$, were immersed in aqueous SO_2 (sulfurous acid) at pH levels of 2.0, 3.0, 4.0, and 5.6 (distilled water) for various times, then were removed, dried, weighed, and analyzed by FTIR-ATR. The weight loss data is shown in Figure 4, and loss of $CaCO_3$ is evident in the infrared spectra shown in Figure 5. Plots of the integrated intensity loss of the $CaCO_3$ infrared peaks at 875 and 1416 cm^{-1} at various pH levels are very similar to Figure 4. The removal of $CaCO_3$ is diffusion controlled at pH = 2.0, with an effective diffusion coefficient of 1.84 x $10^{-9} cm^2/sec$. At higher pH levels, the rate of removal is retarded, presumably because of the increasing contribution of the chemical reaction rate between H^+ and $CaCO_3$, which would decrease with decreasing $[H^+]$ (increasing pH). Given sufficient time, all of the $CaCO_3$ is removed from the paint films (total weight loss = 27%), even with distilled water, which is somewhat acidic because of reaction with atmospheric CO_2 to form carbonic acid. In contrast, very little weight loss (7% maximum) was noted for the paint without $CaCO_3$. The polymer IR spectra showed essentially no changes, even after a one-month immersion in pH 2.0 sulfurous acid. Immersion of the $CaCO_3$-containing paint for a fixed time in 10 different acids and acid mixtures at pH 3.0 produced essentially the same weight loss as pH 3.0 sulfurous acid.

A real-time method FTIR-ATR method was developed to monitor diffusion and chemical reactions occurring in the paint films simultaneously. Re-

sults for the $CaCO_3$-containing latex paint are shown in Figure 6. Selected IR bands corresponding to $CaCO_3$, water, and the polymer were followed with time upon exposure to sulfurous acid at pH 1.3. The water peak intensity (O-H stretch) passes through a maximum with time, whereas the polymer peak intensity (C-H stretch) goes through a minimum before leveling off. The $CaCO_3$ data represents the amount removed; this quantity reaches its constant maximum value (100% loss of $CaCO_3$) just before the water and polymer peaks reach their extreme values.

The decrease in the polymer peak intensity indicates polymer swelling. The amount of swelling increases proportionately to the amount of water sorbed; plots of water peak intensity against polymer peak intensity show linear behavior. However, after removal of the $CaCO_3$, the polymer deswells, presumably to fill in the voids left by removal of the $CaCO_3$ particles. A corresponding amount of water is "squeezed out" by the deswelling of the polymer. Similar experiments conducted with the latex paint without $CaCO_3$ and for the latex polymer base did not exhibit this deswelling behavior. When the paint film is attached to a rigid (wood) substrate, collapse of the film upon loss of $CaCO_3$ may constrain the film so as to produce a reduction in film thickness. The thickness reduction would be about, 16% which is the volume percent of $CaCO_3$ in this paint. A decrease in the film thickness may also result in a proportional increase in the flux of SO_2 or any other species through the film (Eq. 3).

It has also been found that removal of the $CaCO_3$ causes a reduction in the dynamic modulus of the paint above its glass transition temperature (2).

Whether this has a detrimental effect on the performance of the paint has not yet been established.

PAINT-WOOD INTERFACE STUDIES

In an earlier study, western redcedar (Thuja plicata) panels were exposed outdoors for up to 16 weeks prior to being painted. This brief exposure sufficiently weathered the wood surface to inhibit proper paint adhesion when panels were subsequently painted with either an oil-alkyd or acryliclatex primer. Paint adhesion decreased with exposure time. Paint adhesion to panels exposed for 16 weeks decreased 50% compared with adhesion to panels not exposed prior to painting. A more detailed description of this work has been previously reported (9). Sulfurous acid, sulfuric acid, and nitric acid were found to increase the rate of wood degradation. Sulfurous acid increased the rate of wood weathering by 50% compared with that of control specimens exposed to distilled water (10).

In this study, the EDS analysis of WRC panels (Fig. 7) and EDS sulfur analyses (Fig. 8) of SP panels painted with acrylic-latex primer and topcoats showed sulfur accumulation at the paint-wood interface during accelerated weathering exposure (11). For both WRC and SP specimens painted with alkyd primer and topcoat, sulfur was detected in specimens treated with sulfurous acid but not in those treated with sulfuric acid (Fig. 9). Results were similar for specimens coated with acrylic-latex paints. Sodium sulfate treatment did not cause sulfur accumulation. The results clearly show that for both alkyd and acrylic latex paints, SO_2 and/or sulfurous acid readily diffuse in the wood surface, whereas sodium sulfate and sulfuric acid do not. Results from panels exposed to

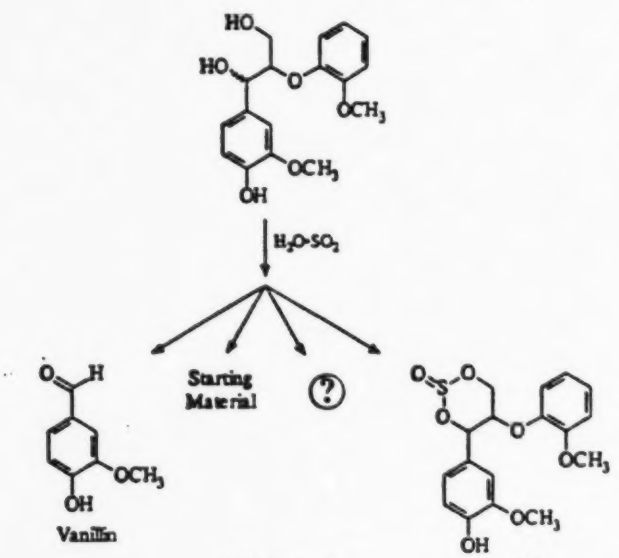
sodium sulfite were not consistent. We should continue to evaluate sulfuric acid because voids may occur in good paint systems after a short exposure time, particularly on wood substrates because of the extreme moisture-induced dimensional changes in wood.

One brief SO_2 sorption-desorption experiment was conducted with a thin slab of wood (WRC). The wood sorbed about 80% by weight of SO_2 at 367 torr, and retained 18% of the amount sorbed after exposure to vacuum. Thus, it appears that SO_2 also reacts extensively with this type of wood. This finding is consistent with the SEM and EDS results (11).

Chemical Analysis

Lignin was isolated from solvent-extracted WRC specimens exposed to SO_2 and from a control exposed to 100% RH. The ^{13}C-NMR spectra of the acetylated lignins are shown in Figures 10A and 10B. Differences occurred in several areas of the spectra. The signal from the acetylated phenolic hydroxyls (170 ppm) in the lignin from treated specimens increased substantially relative to those signals for α and γ hydroxyls. This indicates extensive depolymerization (or β-ether cleavage) of the lignin isolated from the specimen treated with SO_2. In the region of 60 to 80 ppm, representative of the α and β carbons of the lignin C-9 units, significant changes occurred. The β signal diminished in the treated sample with a concomitant new group of signals around 70 ppm. Signals arising from the α carbons at about 75 ppm were also diminished. These changes in the aliphatic region of the spectrum might be caused by reactions of the sulfur species with the lignin sidechain. The region at 100 ppm (±5 ppm) in the treated lignin spectra showed two new broad

peaks, which were probably caused by an appreciable amount of degraded carbohydrate material extracted along with the lignin. These carbyhydrates would also contribute to secondary acetate carbonyl signals overlapping with the lignin acetylated hydroxyl signals in the 170-ppm region. The lignin models were synthesized as described by Landucci et al. (12) and are shown in Scheme 1. The ^{13}C-NMR of the acetylated model I is shown in Figure 10 C. Four samples of model compound were subjected to the same conditions as the treated specimens of lignin and were sampled at 1, 2, 7, and 14 days, respectively. The model compound was basically intact after two days, but the seven-day sample showed some losses of predominantly the erythro form. After acetylation to stabilize the products, about 15 mg (10%) of a new compound was isolated and tentatively identified as compound III, based on ^{13}C-NMR and mass spectroscopy (Scheme 2). The remaining material (10%), other than unreacted starting material, consisted of several compounds in small amounts and was not identified, although the smell of vanillin was detected.



Scheme 2

The specimen that was treated for 14 days contained 16% starting material, 8% compound III, and a mixture of compounds as seen in the 7-day sample. Further experiments are underway to isolate and identify the remaining unknown compounds.

A typical example of softwood lignin structure is shown in Figure 14; C-9 units are enclosed in boxes (2). The models used in our work closely approximate these units. The ^{13}C-NMR spectra of the acetylated model I and of the lignin isolated from WRC specimens are labeled to show corresponding α, β, and γ carbons (Figures 10A and 10C). A cursory comparison of the ^{13}C-NMR spectra of the new compound and the treated lignin indicated that this was not a major degradation product in the treated lignin. Because the concentration of compound III decreased from 7 to 14 days after treatment, this compound may be an intermediate. Experiments underway involve larger scale treatments for longer times in SO_2 atmospheres and in sulfurous acid so that the other degradation products can be isolated for identification.

The model compound II with the phenolic hydroxyl blocked with a methyl group will be treated in the same way as compounds in previous model studies. Many C-9 units in lignin are esterified at this phenolic position (Fig. 11), and compound II may play a role in the degradation pathways. When the degradation pathways and products have been elucidated, this information will be used to interpret the chemical and structural changes that occur in treated lignin specimens and ultimately in field trial specimens.

Adhesion Testing

The shear strength of painted wood specimens treated with SO_2 and the controls are shown in Figure 12. The bars show the standard deviation. The large coefficient of variation (COV) apparent in this plot was caused by the large variability of the wood and the large amount of wood failure in the specimens. The strength of the paint bond was controlled more by the board the specimen was cut from than the acid treatment. This board-to-board variability completely obscured any changes caused by treatment. Much of this variability can be avoided by using a more sensitive test procedure. Uniform double cantilever beam (UDCB) specimens were tested by using fracture mechanics techniques. For comparison, two sets of specimens were prepared from the same panel. The adhesive strength for shear specimens was 5.50 mPa ± 0.17 (COV = 3.7) and for UDCB specimens, 281.8 ± 6.6 J/m^2 (COV = 2.4). We were able to limit crack propagation completely to the paint-wood interface with the UDCB specimens. In previous paint adhesion tests, the controls and many treated specimens failed primarily in the wood substrate.

SECTION 4

CONCLUSIONS

The major findings of the study on the effects of acidic deposition on painted wood substrate systems are summarized in the following conclusions:

- Our Fourier-transform infrared (FTIR), nuclear magnetic resonance (NMR), sol-gel, and intrinsic viscosity results demonstrate that SO_2 (in the presence of UV light) can react chemically with the base polymer in acrylic latex paints, and thus accelerate the rate of degradation of the coating.

- The latex paint coating is a poor barrier to SO_2 and will not prevent diffusion of SO_2 to the wood substrate, where additional chemical reaction and degradation may take place.

- Results of preliminary sorption experiments for SO_2 in thin wood suggest that SO_2 is chemically reacting with the wood. This is consistent with scanning electron microscope (SEM) data, which shows accumulation of sulfur at the paint-wood interface after soaking painted wood samples in sulfurous acid. More recent NMR data shows direct evidence for chemical reaction of SO_2 with wood. The consequences of these results as far as paint-wood adhesion is concerned are currently being investigated.

- Data from desorption experiments conducted with alkyd paint show retention of about 10-20% of the sorbed SO_2. This indicates that a chemical reaction could be occurring with this paint as well.

- Quantitative data for the rate of removal of the $CaCO_3$ additive from latex paints have been obtained as a function of pH by using sulfurous acid. All of the $CaCO_3$ is removed from a 5-mil-thick paint film in about 4 h at pH 2.0, 60 h at 3.0, and 430 h at pH 4.0. Distilled water equilibrated with atmospheric CO_2 (pH 5.6) has also been shown to remove all of the $CaCO_3$, but it takes about 40 days.

- $CaCO_3$ removal is accompanied by a collapse of the polymer to fill in voids previously occupied by the $CaCO_3$ particles. If the film is attached to a rigid wood substrate, this collapse would be constrained so as to produce a decrease in the film thickness. The reduction in thickness is estimated at 16%; this is the volume percent of $CaCO_3$ in the paint film. Loss of $CaCO_3$ will increase the SO_2 solubility and perme-

ability of the paint, and the decrease in thickness will cause a further increase in the flux of SO_2 or any other species through the film.

- Separate swelling experiments with the latex paint and water have been conducted. Considerable swelling of the paint film (about 14%) occurs when immersed in water.

- Fracture mechanics is a promising technique for testing paint adhesion to wood. The coefficient of variation of the data is within the 4-6% range.

SECTION 5

RECOMMENDATIONS

The following recommendations are made regarding future exposure studies:

- Conduct exposures of coatings-wood substrate systems in environmental chambers at North Carolina State University (Raleigh, NC), U.S. Environmental Protection Agency (Research Triangle Park, NC), and Forest Products Laboratory (Madison, WI) at atmospheric pollutant levels to develop dose-response relationships. Generic coatings that represent commercial coatings of known ingredients should be used in these exposure studies. These investigations should be directed to the discoloration or "yellowing" of coatings and the loss of film-substrate strength that may result in blistering and peeling of latex coatings, formulated with and without $CaCO_3$ that are applied to Southern pine and Western red cedar substrates.

- Continue short-term exposures of base acrylic latex (supplied by a major producer) and commercial paints on wood substrates and free films. These tests would serve as a guide for establishing degradation mechanisms and for designing chamber exposures under atmospheric pollutant levels.

- Design and conduct a field exposure study using covering-spray devices at the Research Triangle Park, NC, and Steubenville, OH materials exposure sites to investigate the formation of mildew associated with the loss of ZnO, the discoloration or yellowing

of $CaCO_3$ containing paints, and the loss of film substrate strength (peeling, etc.). This study would complement and support the chamber exposure studies.

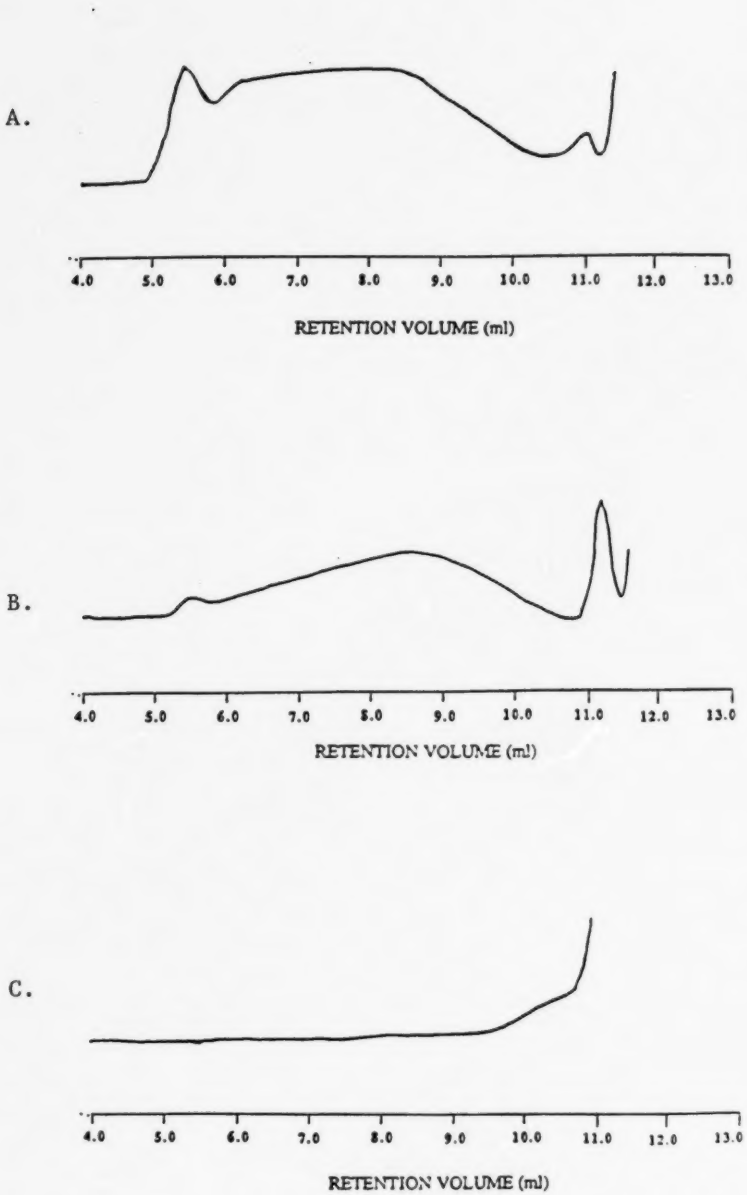


Figure 1 GPC Chromatogram of Base Acrylic Polymer

A. Unexposed Film B. Exposed Film to UV/Air for 96 h

C. Exposed Film to UV/SO_2 for 96 h

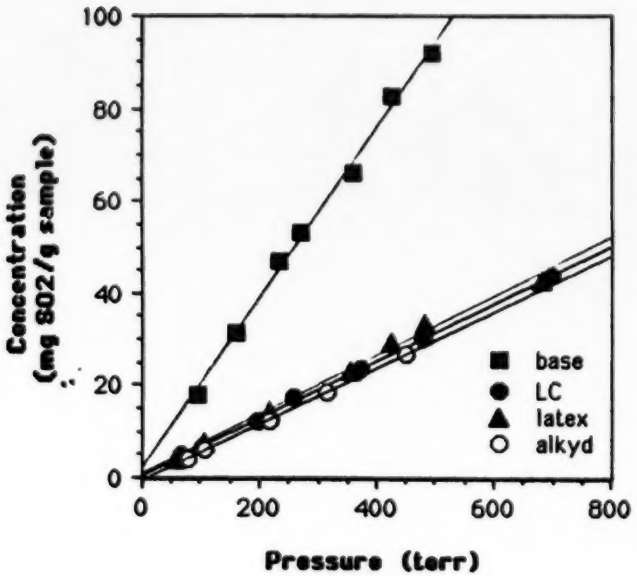


Figure 2 Sorption isotherms for SO_2 in paint samples at 28°C

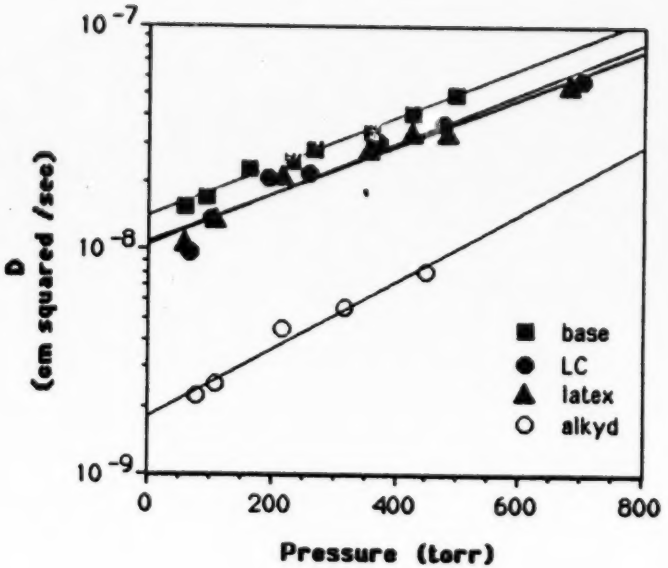


Figure 3 Diffusivities of SO_2 in paint samples at 28°C

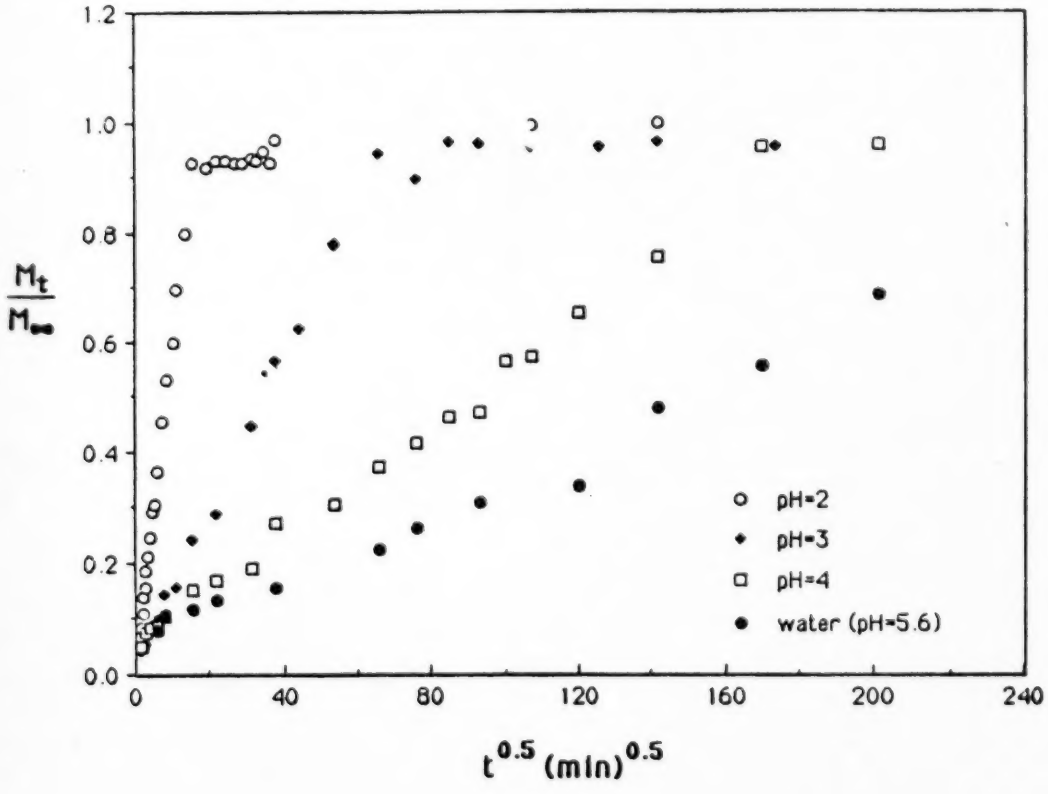


Figure 4 Weight loss of $CaCO_3$ from latex paint samples in sulfurous acid

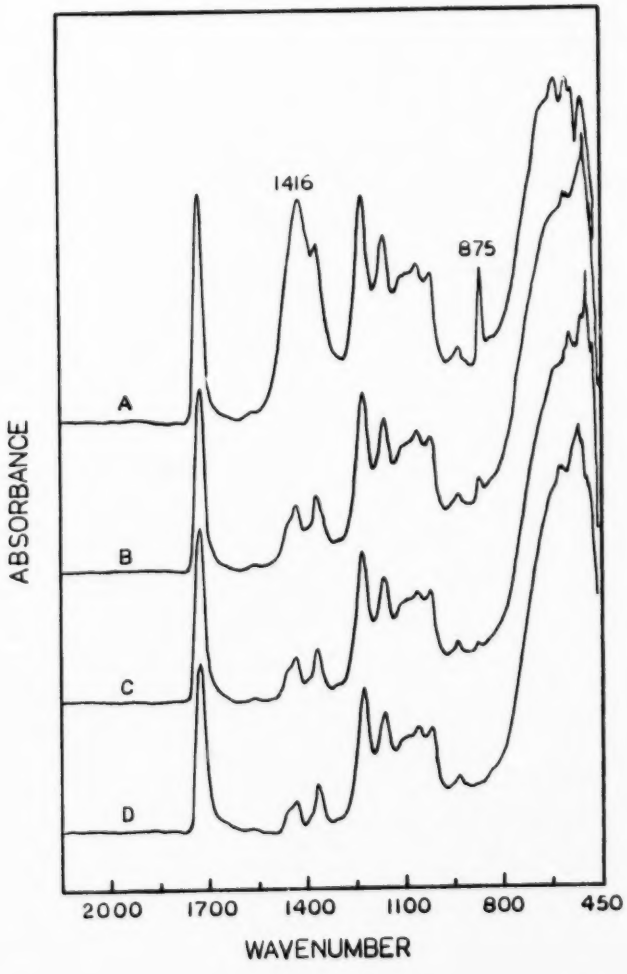


Figure 5 FTIR-ATR spectra from latex paint samples exposed to pH 2.0 sulfurous acid for (A) 0 min., (B) 1 min., (C) 6 min., (D) 30 min.

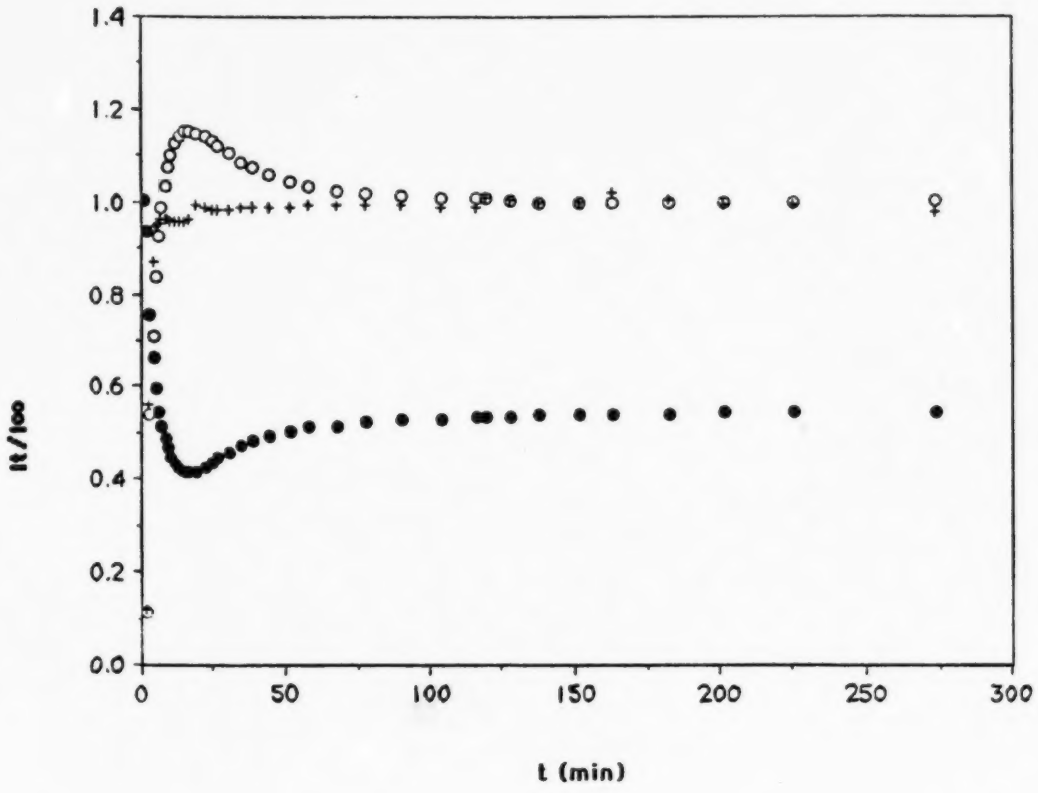


Figure 6 Relative infrared peak intensities for latex paint immersed in pH 1.3 sulfurous acid. Open circles: water uptake, closed circles: polymer peak intensity (C-H stretch at about 3000 cm^{-1}), crosses: loss of $CaCO_3$

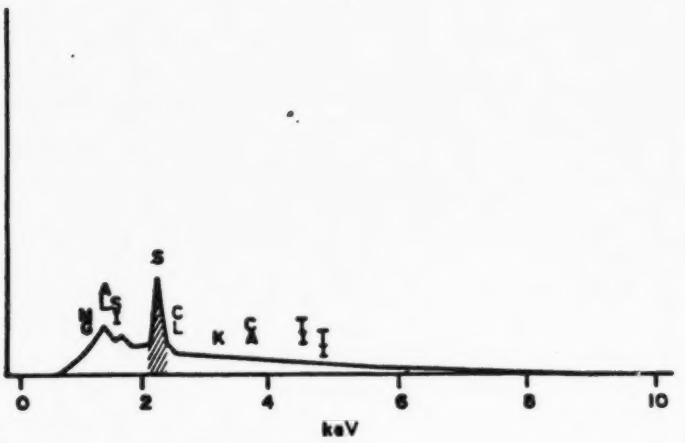


Figure 7 EDS of the cross section of WRC panels treated with sulfurous acid showing elemental constituents just below paint-wood interface. Vertical full scale is 4,096 counts.

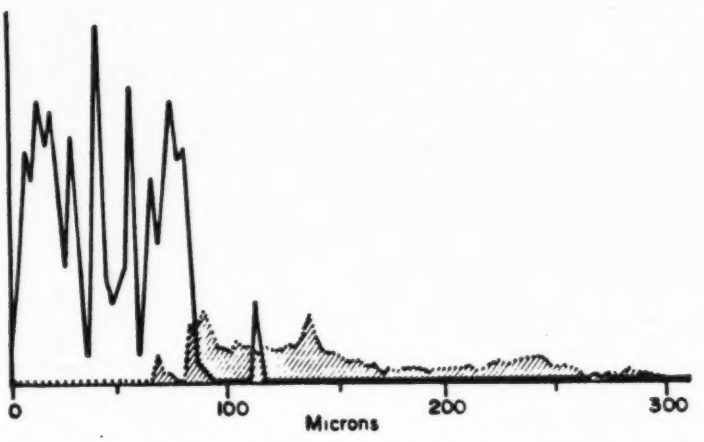


Figure 8 EDS line scan of sulfurous-acid-treated SP panels painted with one coat of acrylic-latex primer and two top-coats. Titanium ——— Sulfur ..... Vertical full scale = 10,643

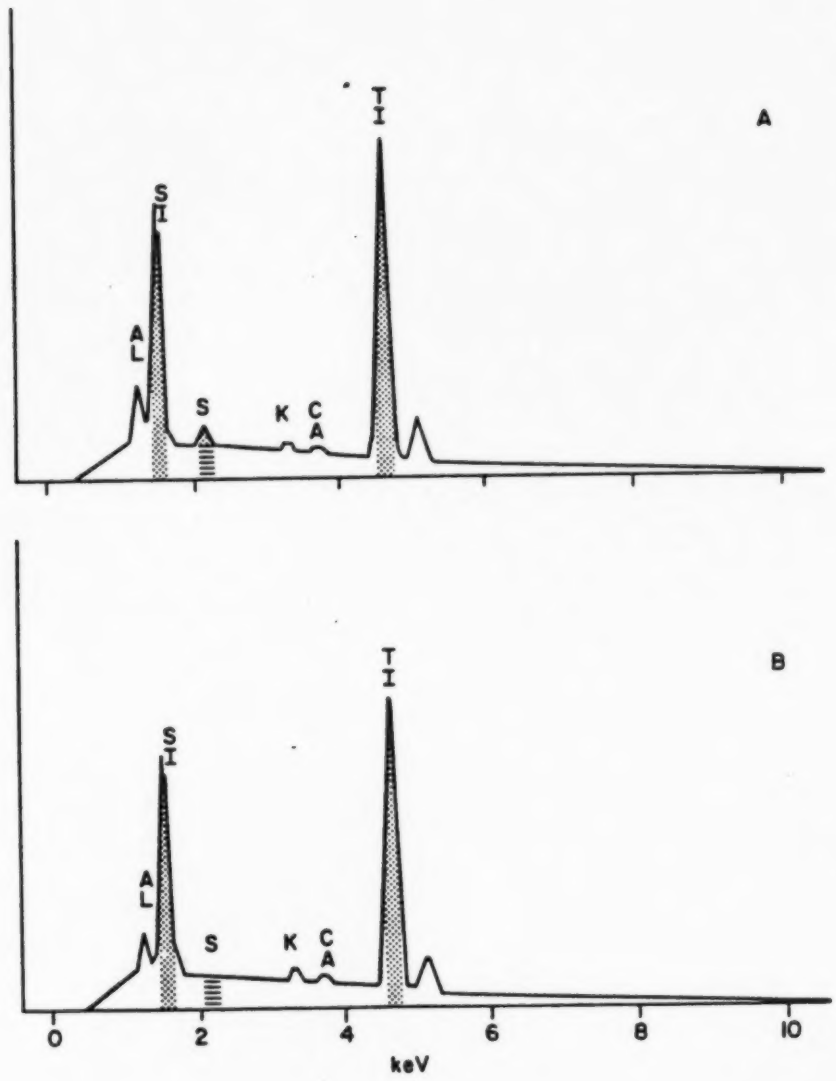


Figure 9 EDS of paint-wood interface of WRC painted with oil-alkyd primer and topcoat. A, treated with sulfurous acid. B, treated with sulfuric acid

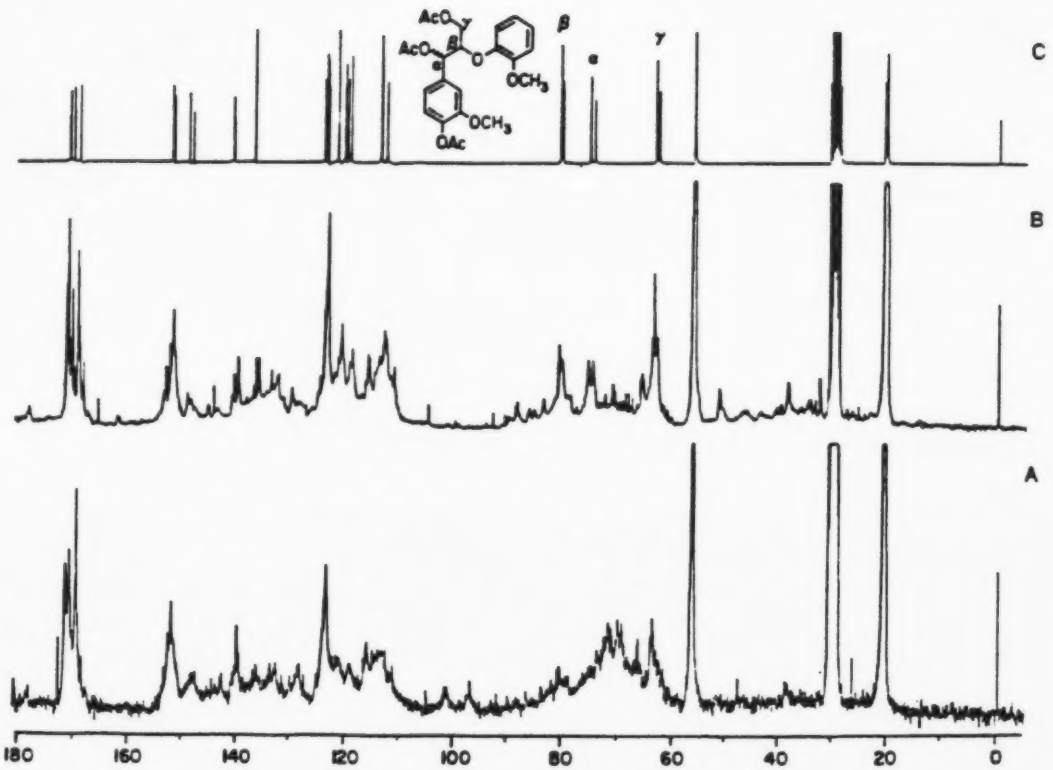


Figure 10 A ^{13}C-NMR of lignin extracted from WRC treated with sulfurous acid, B Control treated with water, C Lignin model compound I

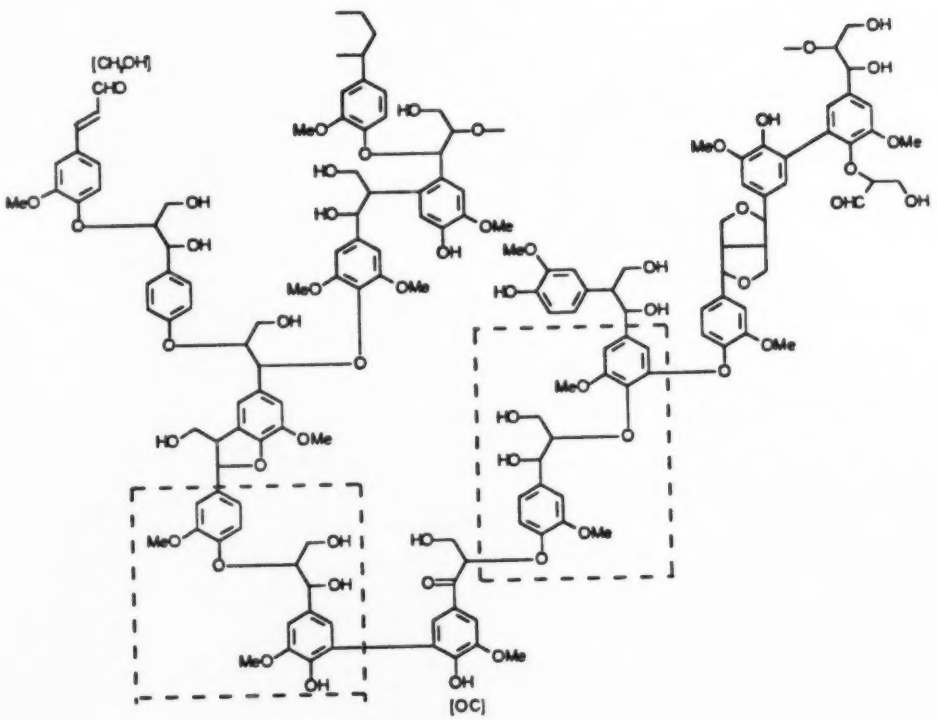


Figure 11 Typical structure for softwood lignin; structure of model compounds shown in boxes

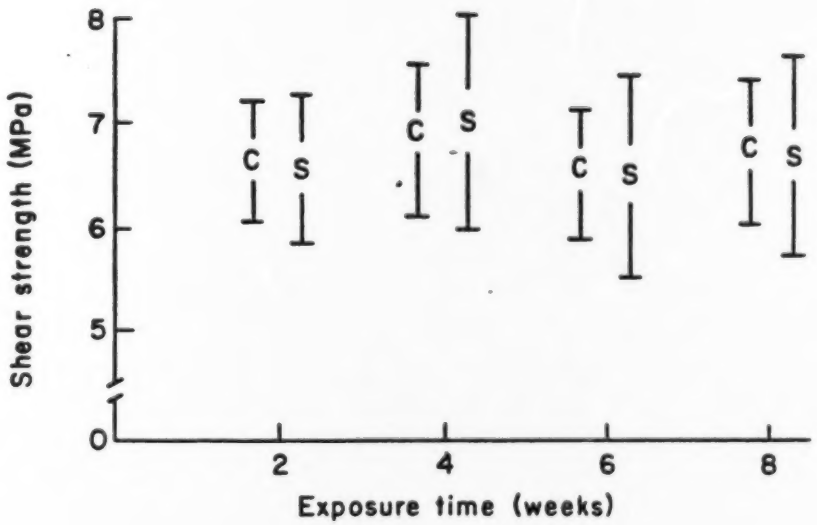


Figure 12 Adhesive strength of painted specimens exposed to 100 ppm sulfur dioxide for up to eight weeks and their matched controls. C, Control; S, treated specimen

TABLE 1. COMPOSITION (% BY WEIGHT) OF PAINTS

Paint Component	Alkyd	Latex	Latex
Pigment			
ZnO	2.5		
$CaCO_3$	7.5	12.7	
TiO_2	25.0	21.2	25.4
China Clay		4.2	12.7
Vehicle			
Soya/Phthalic Copolymer	48.8		
Mineral Spirits	12.0		
H_2O		20.5	20.5
Latex Emulsion		35.0	35.0
Butyl Cellosolve	2.5		
Driers	.4		
Additives	1.7	4.0	4.0
Ethylene Glycol		2.4	2.4

TABLE 2. PROPERTIES OF THE BASE POLYMER OF A LATEX PAINT UPON EXPOSURE TO SO_2/H_2O/UV COMBINATIONS

# Sample Castings	UV Exposure, 350 nm # (hrs)	SO_2 (mL/mm)	[n] [dL/g]	Contact Angle (deg.)	Gel (%)	T_g (°C)
		dry exposure				
5	0	0	1.00	77	22	23
4	48	0	0.77	72	32	23
4	96	0	0.48	72	58	28
4	48	2	0.47	49	64	78
4	96	2	0.13	0	64	87
4	0	2/48 h	1.00	74	22	25
4	0	2/96 h	1.00	76	21	23
		wet exposure				
1	48	0	1.00	79	21	25
1	96	0	0.70	83	22	14
1	48	2	0.04	40	64	49
1	96	2	0.07	0	58	60
1	0	2/48 h	1.10	80	18	40
1	0	2/96 h	0.95	79	20	7

TABLE 3. SOLUBILITY (S), DIFFUSIVITY (D_o), AND PERMEABILITY (P_o) AT TYPICAL ATMOSPHERIC LEVELS OF SO_2

Sample	S (mg SO_2/g sample-torr)	$D_o \times 10^9$ (cm^2/s)	$P_o \times 10^9$ $\frac{cm^3 SO_2(STP)cm^2}{cm^3 sample\text{-}cm\ Hg\text{-}s}$
Latex polymer base	0.189	14.2	12.1
Latex with $CaCO_3$	0.0622	10.6	4.88
Latex without $CaCO_3$	0.0681	10.9	5.52
Alkyd	0.0607	2.59	1.16

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